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(54) Name of the invention:

Vinyl Chloride Type Resin Film

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*[Note: Names, addresses, company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified by a numeral prefix or a general form of plurality suffix.]*

## **(54) [Name of the Invention]**

### **Vinyl Chloride Type Resin Film**

## **(57) [Abstract]**

### **[Objective]**

The objective of the present invention is to suggest a vinyl chloride type resin film appropriate as a substrate material film for stainless steel or steel plate etc., surface protection films, marking films, masking films, etc.

### **[Structure]**

Vinyl chloride type resin obtained as a resin composition material, obtained as hydrotalcite compound, fatty acid zinc compound,  $\beta$ -diketone compound, acrylic type resin and a plasticizing agent are added to vinyl chloride type resin, is formed into a film material.

### **[Scope of the Claims]**

#### **[Claim 1]**

Vinyl chloride type resin obtained as a resin composition material, obtained as hydrotalcite compound in an amount in the range of 0.3 ~ 3 weight parts, fatty acid zinc compound in an amount in the range of 0.1 ~ 2 weight parts,  $\beta$ -diketone compound in an amount in the range of 0.02 ~ 0.5 weight parts, acrylic type resin in an amount in the range of 1 ~ 50 weight parts and a plasticizing agent are added to 100 weight parts of vinyl chloride type resin, is formed into a film material.

#### **[Claim 2]**

Adhesive (tacky) vinyl chloride type resin film obtained as an adhesive agent layer is provided on at least one surface of the vinyl chloride type resin film according to the above claim 1.

### **[Detailed Explanation of the Invention]**

#### **[Technological Field of Application]**

The present invention is an invention about a vinyl chloride type resin film that is appropriate for use as a substrate material film for insulation tape, stainless steel, steel plate, plywood board, etc., protective films, marking films, or masking films, etc., and about the adhesive film using this substrate material.

[0002]

#### **[Prior Art]**

The stainless steel, steel plate etc., surface protective films, marking films, masking films, etc., are films with a basic structure where an adhesive agent layer is layer laminated on a substrate material film, and the condition whereby at the time when these are separated from the material subject to the adhesion, there is no adhesive agent remaining adhered onto the material subject to the adhesion, namely, that the interfacial adhesive force between the substrate material film and the adhesive agent layer, is higher than the interfacial adhesive force between the adhesive agent layer and the material subject to the adhesion. However, in the case when vinyl chloride type resin film is used as the substrate material film, because of the transfer of the plasticising agent, which is a compounded agent for plastification, the interfacial adhesive force between the substrate material film and the adhesive agent layer is decreased, or the cohesive strength of the adhesive agent itself is decreased, and there have been significant problems.

[0003]

As measures in order to solve this problem, the method using a polyester type plasticising agent where the plasticising agent transfer is small, or the method where an undercoating treatment is performed on a soft vinyl chloride type resin film, have been used. However, in the case of the used for a long period of time marking film, or masking films, which are exposed to high temperatures at the time when they are baked together with the automobile body during the painting operation, still higher product quality is required, and according to the previous technology it has been difficult to respond to these requirements.

[0004]

#### **[Problems Solved by the Present Invention]**

The authors of the present invention have conducted rigorous studies in order to solve the above described problems, which occur in the case when the substrate material film is made of vinyl chloride type resin film, and as a result from that, they have found that the epoxy compounds and phosphorous acid ester compounds, usually used in the previous technology as stabilizing agents for the vinyl chloride type resins, cause the deterioration

of the interfacial adhesive force etc., properties of the adhesive agent, and especially, as results from studies, they have observed that by selecting specific compounding agents, even if the epoxy compound and the phosphorous acid ester compounds, are not used, sufficient stability properties are obtained, and the decrease of the interfacial adhesive force is also suppressed and the present invention was completed.

[0005]

#### [Measures in Order to Solve the Problems]

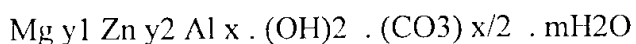
However, the indicated by the present invention essential element exists in a vinyl chloride type resin film obtained as a resin composition material, obtained as hydrotalcite compound in an amount in the range of 0.3 ~ 3 weight parts, fatty acid zinc compound in an amount in the range of 0.1 ~ 2 weight parts,  $\beta$ -diketone compound in an amount in the range of 0.02 ~ 0.5 weight parts, acrylic type resin in an amount in the range of 1 ~ 50 weight parts and a plasticizing agent are added to 100 weight parts of vinyl chloride type resin, is formed into a film material.

[0006]

As the vinyl chloride type resin according to the present invention it is possible to use besides polyvinyl chloride, also, copolymer materials obtained by using vinyl chloride as the main material and also using other co-monomers, and also mixtures of these materials, or mixtures of these materials and other copolymers or polymers, can be used. The hydrotalcite compound is represented according to the following here below general formula, and it is a composite salt compound, which is formed from a magnesium and aluminum or zinc, magnesium and aluminum, and it is also a good option if it is a material where the crystalline water has been eliminated.

[0007]

[Formula 1]



(where,  $0 < x \leq 0.5$ ,  $y_1 + y_2 = 1 - x$ ,  $0.1 < y_1 < 1$ ,  $0 \leq y_2 < 0.8$ ,  $0 \leq m \leq 2$ )

[0008]

The above described hydrotalcite compound is compounded in an amount in the range of 0.3 ~ 3 weight parts, relative to 100 weight parts of the vinyl chloride type resin material. Especially, it is preferred that it is compounded in an amount that is in the range of 1 ~ 2.5 weight parts. When the amount of the hydrotalcite compound is less than 0.3 weight parts, the thermal resistance properties at the time of the processing are deteriorated. And at a level of 3 weight parts sufficient thermal resistance properties during the processing are demonstrated.

[0009]

As the fatty acid zinc salt according to the present invention, it is possible to use zinc 2-ethyl hexoate, zinc laurate, zinc stearate, etc., high homologous order fatty (aliphatic) acid zinc salts. Regarding the compounding amount of the above fatty acid zinc salts, it is in the range of 0.1 ~ 2 weight parts relative to 100 weight parts of the vinyl chloride type resin, and especially preferably, it is in the range of 0.2 ~ 1.5 weight parts. In the case when the compounded amount of the fatty acid zinc salt is less than 0.1 weight parts, the coloration elimination properties, which are an effect of the  $\beta$ -diketone compound, are deteriorated, and also, in the case when the compounded amount is higher than 2 weight parts, the thermal resistance properties are deteriorated.

[0010]

As the  $\beta$ -diketone compound, it is possible to use benzoyl acetone, dibenzoyl methane, stearyl benzoin methane, etc. The compounded amount of the above  $\beta$ -diketone compound is in the range of 0.02 ~ 0.5 weight parts relative to 100 weight parts of the vinyl chloride type resin, and especially, it is preferred to be within the range of 0.05 ~ 0.4 weight parts. If the amount of the  $\beta$ -diketone compound is less than 0.02 weight parts, the coloration prevention effect, which is due to the joint use with the above described fatty acid zinc salt, is not demonstrated, and if the amount used is higher than 0.5 weight parts, the weather resistant properties are deteriorated.

[0011]

The acrylic type resin that is used according to the present invention is a copolymer material containing methyl methacrylate as its main component and using besides that alkyl methacrylates, alkyl acrylates, acrylic acid etc., co-monomers and copolymerizing these together, and it is a material where the molecular weight is in the range of 50,000 ~ 5,000,000. In more details, for example, Paraloid K (manufactured by Rohm and Haas Company), Metaburene P (manufactured by Mitsubishi Rayon Company), and Kancesu PA (manufactured by Kaneen Chemical Industries Company), etc., polymer materials with a molecular weight that is in the range of 50,000 ~ 100,000, can be used. Depending on the requirements, the acrylic type resin is appropriately compounded in an amount that is in the range of 1 ~ 50 weight parts relative to 100 weight parts of the vinyl chloride type resin. If the amount of the acrylic resin is less than 1 weight parts, the effect of the prevention of the decrease with time of the interfacial adhesive force between the vinyl chloride type resin film, which is the substrate material film, and the adhesive agent layer, is not obtained, and in the case when the compounded amount exceeds 50 weight parts, relative to the obtained effect the acrylic type acid effect is large, and the properties of the vinyl chloride type resin, are deteriorated, and that is why these are not preferred options.

[0012]

After that, as plasticizer agents, phthalic acid ester type, dibasic aliphatic acid ester type, trimellitic acid ester type, and polyester type plasticizer agents, can be used, and these can be selected depending on the applications, however, especially, the so-called non-transferable type plasticizer agents, like trimellitic acid ester type agents, and polyester type plasticizer agents, are preferred. There are no specific limitations regarding the compounded amount of the plasticizer agent, and it can be appropriately determined based on the substrate material film application and on the required flexibility properties, however, usually, it is compounded in an amount that is in the range of 20 ~ 60 weight parts. Besides these, additive agents used in order to impart properties like weather resistant properties, flame retardant properties, anti-oxidation properties, etc., for example, anti-electrostatic agent, ultra-violet ray absorbing agent, flame retardant agent and anti-electrostatic agent, etc., can also be appropriately compounded depending on the application, and it is a good option.

[0013]

It is a good option if for the mixing of the acrylic type resin and the above-described different types of compounding agents into the vinyl chloride type resin, for example, super mixer, ribbon blender, etc., mixing devices known from the previous technology, are used. The mixed resin material obtained this way is formed into a sheet or film etc., shape by using an extruder – molding device, a calender-molding device etc., and by that the substrate material film for the adhesive tape etc., is provided. Here below, the present invention will be explained in further details based on practical implementation examples, however, the present invention is not limited to the described below examples, and these can be modified as long as the essential elements of the present invention are intact.

[0014]

### [Practical Examples]

#### **Practical Examples 1 ~ 4, Reference Examples 1 ~ 5**

##### (1) Formation of the vinyl chloride type resin film

Vinyl chloride type resin composition materials obtained from the compositions indicated in the Practical Examples 1 ~ 4 and the Reference Examples 1 ~ 5, in Table 1, were sufficiently mixed by using a super mixer, and after that they were mixed and kneaded by using a roll heated at a temperature of 170°C, and by using an L-die calender device, they were formed into films with a thickness of 0.1 mm and a thickness of 0.5 mm. However, in the case of the composition materials according to the reference examples, the thermal resistance properties were insufficient, and the resin compositions were degraded and film forming was not possible.

[0015]

## (2) Film evaluation

### 1) Thermal resistance properties

The obtained according to the above described (1) 0.5 mm thick film was placed into an oven at a temperature of 180°C, and the time until it became black, was measured. The results are shown in table 1.

### 2) Coloration prevention properties

The color of the obtained according to the above described (1) 0.1 mm thick film was visually evaluated. The results are shown in Table 1. Moreover, the evaluation presented in table 1 has the described here below meaning.

◎ : extremely excellent

○ : excellent

X : poor

[0016]

### (3) Coefficient of maintaining of the interfacial adhesive force

Adhesive acrylic copolymer material obtained as 45 weight parts of ethyl acrylate, 5 weight parts of acrylic acid, 45 weight parts of 2-ethyl hexyl acrylate, and 5 weight parts of vinyl acetate, were copolymerized, was made into solution by using ethyl acetate, and it was coated on the 0.1 mm thick film obtained according to the above (1), by using a bar coater, and it was dried inside an oven at a temperature of 130°C, and by that an adhesive vinyl chloride type resin film with a 25 micron thick adhesive agent layer provided on it, was obtained. On the adhesive agent layer surface of this adhesive film, a polymethyl methacrylate resin film, was glued, and by using extension testing device, the separation of the two films was caused, and the interfacial adhesive force between the vinyl chloride type resin film and the adhesive agent layer, was measured (this is denoted as “interfacial adhesive force 1”).

[0017]

Also, the above described material with the glued on it polymethyl methacrylate resin film, was placed for 7 days in an oven at a temperature of 70°C, and it was subjected to a thermal treatment, and then it was naturally cooled and after that, by using the same tension testing device the separation between the two films was caused, and the interfacial adhesive force between the vinyl chloride type resin film and the adhesive agent layer, was measured (this is denoted as “interfacial adhesive force 2”). Due to the fact that the polymethyl methacrylate resin film and the adhesive agent layer were strongly adhered, there was no separation of this interface even by this separation procedure. After that, the coefficient of maintaining the interfacial adhesive force was obtained from the interfacial adhesive force 1 and the interfacial adhesive force 2,

according to the following here below formula. The results are shown in table 1. The higher the coefficient of maintaining the interfacial adhesive force is the smaller the decrease of the interfacial adhesive force with the passing of the time, becomes.

[0018]

[1]

Coefficient of maintaining the interfacial adhesive force (%) = [interfacial adhesive force 2 (kg/cm)/ interfacial adhesive force 1 (kg/cm)] x 100

[0019]

{Table 1}

表-1

	実施例				比較例				
	1	2	3	4	1	2	3	4	5
PVC (平均重合度: 1050)	100	100	100	100	100	100	100	100	100
成分組成物									
1 2 3 4 5 6 7 8 9 10 11 12	30	30	-	30	30	30	30	30	30
13	-	-	30	-	-	-	-	-	-
14	-	-	-	-	-	-	3.0	-	-
15	2.0	2.0	2.0	1.0	0.2	2.5	-	2.0	2.0
16	1.5	1.5	1.5	0.8	0.8	-	0.5	0.8	1.5
17	0.4	0.4	0.4	0.2	0.2	-	0.1	0.2	0.4
18	-	-	-	-	-	-	2.0	-	-
19	-	-	-	-	-	-	0.5	-	-
20	-	-	-	-	-	-	0.3	0.3	-
21	-	30	30	30	30	30	30	30	-
22	1.0	-	-	-	-	-	-	-	-
23	70	95	90	95	-	85	10	50	60
24	140	160	160	100	-	140	140	180	140
25	○	○	○	○	-	x	○	○	○

Headings in Table 1:

1. Practical Examples, 2. Reference Examples, 3. PVC (average polymerization degree: 1050), 4. resin composition components, 5. Arugamizer -1 (4\*), 6. zinc stearate, 7. dibenzoyl methane, 8. Ba-Zn type liquid state stabilizing agent, 9. barium stearate, 10. tris nonyl phenyl phosphite, 11. Methaprene P570 A (5\*), 12. Methaprene P551 (\*6), 13. Film evaluation, 14. adhesive force maintaining coefficient (%), 15. thermal resistance properties (minutes), 16. coloration properties.

\*1 polyester type plasticizer manufactured by Mitsubishi Kasei Vinyl Company  
 \*2 trimellitic acid ester type plasticizer manufactured by Mitsubishi Kasei Vinyl Company  
 \*3 Epoxylated soybean oil manufactured by Asahi Denka Company  
 \*4 hydrotalcite compound manufactured by Kyowa Chemical Industries Company  
 \*5 Acrylic type resin manufactured by Mitsubishi Rayon Company  
 \*6 Acrylic type resin manufactured by Mitsubishi Rayon Company



[0020]

**[Results From the Present Invention]**

The vinyl chloride type resin film according to the present invention is a material that has excellent both thermal stability properties and coloration prevention properties even without compounding the epoxy compound and the phosphorous acid ester compound, which have been required according to the previous technology. Also, in the case when it is used as a substrate material film, the decrease of the interfacial adhesive force at the interface with the adhesive agent layer, with the passing of the time, is small, and there is no remaining glue on the material subject to the adhesion, and because of that, it can be appropriately used in marking films that are used for prolonged periods of time or in masking films, exposed to high temperatures, etc.

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